

# A Novel Buffer Layer of CrN for GaN Epitaxy and Optical Device Application

著者	李 錫雨
号	52
学位授与番号	3910
URL	<a href="http://hdl.handle.net/10097/37626">http://hdl.handle.net/10097/37626</a>

	い そっう
氏 名	李 錫雨
授 与 学 位	博士 (工学)
学位授与年月日	平成19年 12月 12日
学位授与の根拠法規	学位規則第4条第1項
研究科, 専攻の名称	東北大学大学院工学研究科 (博士課程) 応用物理学専攻
学 位 論 文 題 目	A Novel Buffer Layer of CrN for GaN Epitaxy and Optical Device Application (GaN 単結晶膜成長のための新しい CrN バッファー層開発とその光デバイス応用)
指 導 教 員	東北大学教授 八百 隆文
論 文 審 査 委 員	主査 東北大学教授 八百 隆文 東北大学教授 松岡 隆志 東北大学教授 山根 久典 東北大学准教授 曹 明煥

## 論 文 内 容 要 旨

Most of GaN applications have been based upon thin GaN films grown on dissimilar substrates. Therefore, the quality of the GaN films is dependent on the properties of the substrate. Among the substrates, sapphire substrates have been most widely used, since some of the best available performances have been achieved on sapphire substrates. However, sapphire substrates have large lattice and thermal expansion coefficient (TEC) mismatches. Hence the growth of high-quality GaN films on sapphire substrate is of primary importance. Furthermore, low electrical conductivity of sapphire substrate requires a special device structure. Thus, most of GaN-based devices should have employed top contact (horizontal) device structures. Besides, sapphire substrates have low thermal conductivity; hence the device structure with sapphire substrate restricts effective heat removal from the device: Active-region in the device is easily overheated, and then output efficiency decreases. In order to overcome the low heat dissipation, one of the most desirable device structure is a vertical device structure, which can be fabricated by bonding the device onto another high heat-dissipation substrate followed by detaching from the original sapphire substrate. As a result, in order to realize reliable and high-efficiency devices, 1) high quality GaN films with low dislocations and 2) effective heat removal from the active layer in devices are extremely desirable.

In this study, in order to achieve these two requirements, we introduce novel CrN buffer for GaN epitaxy and GaN-based optical devices as well. The advantages are as follows; 1) lattice and TEC matched CrN buffer layer enables high quality GaN films on sapphire substrate, 2) chemically etchable CrN can offer a high heat dissipation method by adopting a vertical device structure.

This thesis consists of nine chapters.

In **Chapter 1**, the overview of III-Nitrides semiconductors, physical properties of GaN, substrates and buffer layers for GaN epitaxy, and problems of GaN-based devices are described. The methods and studies for solving these problems are discussed. At the end of the chapter, the purpose of this study is addressed. The critical problems of GaN based optical devices are that 1) the light degradation and thermal or electrical damage near defect area such as dislocations and 2) an insufficient thermal dissipation from an active layer. In order to solve these problems, high quality GaN crystal with low dislocations and a method for good thermal dissipation are desirably demanded. GaN growth on a suitable substrate, i.e., with the same lattice parameters of GaN and high thermal conductive materials, could be the best way to solve the problems. However, some of the best reliable performances have been achieved on the sapphire substrates due to lack of suitable substrates. Consequently, finding worldwide manufacturer of GaN optical devices are mostly using sapphire substrates. Hence, developing a novel buffer layer with small lattice misfit should be a good method to produce high quality GaN with low dislocations. In order to solve thermal dissipation problem, detaching of a GaN layer from a low-thermal conductive sapphire substrate and its re-attaching on high-thermal conductive materials is one of desirable solution. Hence, a convenient detaching method should be demanded to be a suitable buffer layer. Consequently, this study purposed to introduce a lattice matched and chemically etchable buffer layer for high quality GaN on sapphire substrate. It could be a reliable solution to solve the critical problems of GaN optical devices.

**Chapter 2** focuses on the design of a buffer layer for GaN epitaxy. An appropriate candidate for a novel buffer of GaN films on sapphire are discussed. In order to invest the feasibility of the materials as a buffer layer, a primary experiment with selected materials, i.e., Pt, TaN, TiN, CrN and ZnO, was carried out. When GaN layers were grown on sapphire substrate with Pt and TaN buffer layer, the GaN films had a very rough surface. In case of using TiN, CrN and ZnO buffer layer, the GaN layers had a smooth surface with high crystal quality. However, the presence of misoriented GaN grains in the GaN layers with ZnO buffer layer could be a problem for device applications. The detaching from the sapphire substrate is appropriate solution for manufacturing vertical LEDs with high efficiency. For that convenient separation from sapphire substrate, chemically etchable buffer layer should be demanded. The ZnO and CrN buffer layers were chemically etchable but the TiN buffer layer were could not be detached by chemical wet etching. Empirically, the most suitable material should be CrN. Among the candidates of buffer, the CrN layer is a suitable buffer layer due to the satisfaction of the appropriate material properties as follows; 1) buffer with intermediate lattice-constant between a GaN film and a sapphire substrate, 2) buffer with intermediate-TEC between a GaN layer and a sapphire and 3) materials stable at high temperature. A CrN film has small lattice misfit approximately 6.6% with a sapphire substrate and 8.9% with a GaN film, and

the CrN film has an intermediate thermal expansion coefficient ( $6 \times 10^{-6}/\text{K}$ ) between those of a sapphire substrate ( $6.66 \times 10^{-6}/\text{K}$ ) and a GaN film ( $5.59 \times 10^{-6}/\text{K}$ ).

**Chapter 3** describes the experimental and characteristic apparatus such as the growth system, its principle and characterization methods.

**Chapter 4** focuses on the deposition of a Cr layer on c-sapphire and its structural characterization and directional arrangement with substrate. Growth temperature mainly influences the crystal quality of the Cr layers.  $\text{Al}_2\text{O}_3$  (0001) plane is parallel with Cr (110) plane. The deposition-temperature was adjusted from RT to  $900^\circ\text{C}$ .  $\text{Al}_2\text{O}_3$  (0001) plane is parallel with Cr (110) plane. The increase of Cr (110) and Cr (220) peak-intensity observed for increasing deposition-temperature of Cr layers. The increase of peak-intensity with FWHM and narrowing observed for increasing deposition-temperature of Cr layers. This result suggests that the Cr layer grown at higher temperature have higher crystal-quality. The peak-separations ( $\pm 4.9^\circ$ ) of  $\phi$  scans are enhanced for increasing deposition temperature. These peak separations at high temperature illustrate the change of growth mode from the NW (OR-I) to KS (OR-II).

**Chapter 5** focuses on the firstly attempted formation of a CrN layer on c-sapphire and its structural characterization and directional arrangement with substrate. Nitridation temperature influences the morphology and crystal quality of the CrN layers. As nitridation temperature rises, the surface morphology converts to the trigonal pyramidal shape with three facet planes.  $\text{Al}_2\text{O}_3$  (0001) plane is parallel with CrN (111) plane.  $\text{Al}_2\text{O}_3$  [01-10] direction is parallel with CrN [011] direction. In order to specify the shape of islands, cross-sectional views of CrN/sapphire samples were characterized by TEM. A surface morphology of  $900^\circ\text{C}$ -sample showed comparatively flat surface with a continuous layer. As nitridation temperature rising, the surface morphology converted to typical island-morphology and the height of islands changed 20 nm to 90 nm with facets. In case of CrN, the {100} plane is considered to be of the lowest surface energy because of the following reasons: (1) {100} is an electrically neutral plane (i.e. the same number of cations and anions on the {100} plane), while the {111} planes have all anions or all cations. (2) The dangling bonds of surface atoms on the {100} plane are the smallest. the {100} planes are the most stable planes with the lowest surface energy, therefore CrN {100} planes were remained at higher temperate.

In **Chapter 6**, the optimized condition for better GaN growth on CrN/sapphire is investigated through the characterization of surface morphologies, structural and optical properties. A two-step growth method; 1<sup>st</sup> and 2<sup>nd</sup> step GaN layers are respectively grown at  $900^\circ\text{C}$  and  $1040^\circ\text{C}$ , is very effective to form two dimensional flat surfaces.  $900^\circ\text{C}$ -grown GaN layers have roles of nucleation and columnar growth. The columnar growth involves matching of integral multiple of lattice planes across the film-substrate interface. In addition, high nitridation-temperature enhances a flat GaN surface with a low pit-density. FWHM of XRD and pit density of GaN layers grown on each CrN buffer layers (i.e., 30 minutes-nitrated CrN layer at 900, 1040, 1060 and  $1080^\circ\text{C}$ ) are decreasing as nitridation temperature increasing. The meaning is that the  $1080^\circ\text{C}$ -nitridation has an effect on GaN growth; mirror-like GaN surface without pits and high crystal quality of GaN layers. As a result, a two dimensional flat GaN surface is achieved by control of nitridation temperature and first step growth temperature.

The GaN layers have a typical step-terrace surface and high crystal quality. Three layers have an epitaxial relationship of (0001) Sapphire // (111) CrN // (0001) GaN and [1-100] Sapphire // [10-1] CrN // [11-20] GaN. Typical  $\omega$ -scan FWHM of GaN films on sapphire with CrN buffer layer were 349 arcsec for (0002) plane and 673 arcsec for (10-12) plane. Screw and edge dislocation densities were evaluated by TEM and XRD-estimation. Screw dislocation density was  $2 \times 10^7 \text{ cm}^{-2}$  and edge dislocation density was  $6 \times 10^8 \text{ cm}^{-2}$ , respectively. These results evidence that high GaN crystal quality with low dislocations, and dislocations with screw component are effectively diminished.

**Chapter 7** describes a separation technique, i.e., chemical lift-off (CLO) method. A GaN layer is detached from a substrate by chemical selective etching of a CrN layer. Using this technique, strain relaxation phenomena and the bandgap transition energy with and without strain effect were evaluated. A new equation, which consists of temperature dependence of the exciton transition energy and its strain related temperature shift in the stressed GaN layer, is proposed. In addition, The micro-PL measurement was used to carry out surface scanning of local spot along partially separated and non-etched GaN film to characterize variation of strain in GaN films while the CLO process is progressing. The strain in GaN films is gradually released to bulk-like GaN crystal during CLO. The result indicates that the CLO process is gradually released and reliable method for detaching GaN films from sapphire substrate. CLO technique is very helpful to simultaneously characterize crystallographic and optical properties of strained- and non-strained film on a wafer.

**Chapter 8** focuses on the fabrication of conventional top-contact LEDs and novel V-LEDs. Moreover, this chapter deals with leakage current of GaN-based LEDs to clarify the responsible dislocation types for the forward leakage current. The leakage current of an LED with a CrN buffer layer is less than two orders of magnitude smaller than that of convention LEDs with LT-GaN buffer layers. As a result, it is indicated that the CrN buffer layer has a role of reduction of dislocations. Especially, dislocations with open-core screw component which have strong relationship with leakage current are effectively diminished by inserting a CrN buffer layer.

V-LEDs are demonstrated using the CLO technique. Recently, GaN-based V-LEDs have been in the spotlight due to the advantages of efficient thermal dissipation, high brightness and low operation voltage. In order to achieve the V-LEDs, a method removing from the original substrate is strongly desirable. The novel CLO technique has advantages of damage-free and simple process. Therefore, CLO technique should be a very effective method to fabricate next-generation V-LEDs.

Finally, **Chapter 9** devotes to summarizing and concluding the results.

Consequently, this study purposes to introduce CrN as a lattice-matched and chemically etchable buffer layer for high quality GaN on a sapphire substrate. It is a reliable solution to solve the critical problems of GaN optical devices. Additionally, CLO technique will attract extensive interest in material studies of GaN and technological advantages of a very effective method to fabricate next-generation V-LEDs.

# 論文審査結果の要旨

本論文は窒化ガリウム (GaN) 単結晶膜成長のための新しいバッファ層開発とその光デバイス応用に関する。GaNをはじめとする III-V 族窒化物半導体は、光デバイスあるいは電子デバイスの観点からきわめて有用な物性を持っている。高性能デバイスを開発するためには、高品質膜の結晶成長が基盤となる。格子整合の良い基板が無い窒化物半導体のエピタキシ成長においては、格子不整を緩和するバッファ層が決定的な重要性を持つ。これまで、同族の結晶である GaN や AlN の低温バッファ層により高品質窒化物半導体膜の成長が可能になり、革新的な光デバイス、電子デバイスが創出されてきた。しかし、これらのバッファ層は基板を化学的に剥離できないためデバイス構造に大きな制限があり、基板を化学的手法で剥離できるバッファ層の開発が待たれていた。

本研究は、化学的に基板を剥離でき、しかも極めて高品質の結晶成長を可能とする新しいバッファ層を開発し、そのバッファ層を用いた高品質の GaN 単結晶膜の成長と、化学的に基板を剥離できる特性を活用した画期的な高輝度縦型青色発光ダイオードの作製プロセス (化学リフトオフ法 (CLO: Chemical Lift-off Process)) を開発し、さらに高輝度縦型青色発光ダイオードを作製し、本研究で開発した技術の有効性を示したものである。

本論文は、全 9 章より構成されている。

第 1 章は序論であり、本研究の背景ならびに従来の研究を述べるとともに、研究課題を抽出し本研究の目的を示している。

第 2 章は本研究の根幹をなす窒化物半導体のエピタキシ成長用バッファ層の設計に関する。格子不整、熱膨張係数不整、化学的溶解性、対高温性、窒化特性等種々の観点から種々の物質を物性に基づいて検討し、さらに予備実験に基づく検討を行い、CrN が最適なバッファ層であると結論した。

第 3 章は本研究で用いた実験装置ならびに実験プロセスの詳細に関する。

第 4 章はサファイヤ基板上の Cr 膜の作製と評価に関する。本研究では、工業的な観点から Cr の窒化プロセスによる CrN の作製を検討した。サファイヤ基板上の Cr の結晶性評価に基づき、Cr の最適成膜条件を確立した。

第 5 章は Cr の窒化による CrN の作製に関する。Cr 窒化条件を種々検討し、CrN の結晶性だけでなく、実際に CrN バッファ層上に成長した GaN 膜の結晶評価に基づき、CrN 作製のための最適窒化条件を確立した。

第 6 章は GaN 単結晶膜の高品質化に関する。サファイヤ基板上に形成した CrN バッファ層上への GaN バッファ層の作製と高温 GaN 単結晶膜の作製という 2 段階成長法を開発し、結晶性と表面モフォロジー評価に基づき最適成長条件を確立した。GaN 系デバイスに使用されている GaN 単結晶膜に比べて遜色の無い結晶性を有することを確認した。

第 7 章は CrN バッファ層のエッチングによるサファイヤ基板の剥離技術に関する。成長した GaN 単結晶膜の剥離プロセスにおける評価、剥離後の結晶性、表面モフォロジー評価等から、剥離過程では格子歪が徐々に緩和すること、剥離による結晶性の劣化は無いこと、さらに剥離後のサファイヤ基板の再利用が可能であることを示した。

第 8 章では CrN バッファ層上に作製した青色 LED と縦型高輝度青色 LED の評価を行った。通常の LED に比べてリーク電流の少ない高信頼性の LED が作製できること、縦型 LED では従来型に比べて 10 倍近い高電流動作が可能であることなどを示し、本研究で開発した技術の高輝度縦型青色 LED 作製への有効性を示した。

第 9 章は本研究の結論であり、本研究を総括している。

以上、要するに、本研究は、高品質 GaN 単結晶膜成長における革新的なバッファ層を提示するだけでなく、新たな光デバイス、電子デバイスを可能にするものであり、応用物理学、結晶工学、半導体工学の発展に寄与するところ大である。

よって、本論文は博士(工学)の学位論文として合格と認める。